



DECLARATION

I, Tadashi YAMAMOTO, a national of Japan, c/o Yamamoto International Patent Office of 520 Sanno Urbanlife, 1-8, Sanno 2-chome, Oota-ku, Tokyo 143-0023, Japan do hereby solemnly and sincerely declare:-

- 1) THAT I am well acquainted with both Japanese Language and English language, and
- 2) THAT the attached document is a full, true and faithful partial translation into English made by me of Japanese Patent Publication No. 8-104738A

The undersigned declarant declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Singed this day of February 6, 2006.

Tadashi Yamamoto

Tadashi YAMAMOTO



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Applicant : 000004466

Mitsubishi Gas Chemical Co., Inc.

5-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo

Inventor(s) : Ichikawa Tetushi

c/o Hiratsuka Research Laboratory 6-2,

Higashiyawata 5-chome, Hiratsuka-shi Kanagawa

Seki Kiirou

c/o Hiratsuka Research Laboratory 6-2,

Higashiyawata 5-chome, Hiratsuka-shi Kanagawa

Kono Yutaka

c/o Hiratsuka Research Laboratory 6-2,

Higashiyawata 5-chome, Hiratsuka-shi Kanagawa

(Names of individuals and corporation have been translated  
phonetically)

**【Title of the Invention】** Curing agent for epoxy resin.

**【Abstract】**

**【Object】**The object of the present invention is to provide a curing agent for epoxy resin which can overcome whitening of a curing coating film and can prevent intense whitening generated at the time dropwise added water droplet on a coating film during cure and is excellent in interlayer adhesion in case of double coating.

**【Constitution】** A curing agent for epoxy resin comprising a polyamine compound (A) containing at least one compound selected from xylylenediamine, a modified product obtained by Mannich reaction of xylylenediamine and a phenolic compound or an aldehyde compound, a modified product obtained by the reaction of xylylenediamine and an epoxy compound, a modified product obtained by the reaction of xylylenediamine and a compound having a carboxyl group(s) and a modified product obtained by Michael reaction of xylylenediamine and an acrylic compound and a fatty amine compound (B).

Claims:

1. A curing agent for epoxy resin comprising a polyamine compound (A) containing at least one compound selected from xylylenediamine, a modified product obtained by Mannich reaction of xylylenediamine and a phenolic compound or an aldehyde compound, a modified product obtained by the reaction of xylylenediamine and an epoxy compound, a modified product obtained by the reaction of xylylenediamine and a compound having a carboxyl group(s) and a modified product obtained by Michael reaction of xylylenediamine and an acrylic compound and a fatty amine compound (B).
2. The curing agent for epoxy resin according to claim 1, wherein 2 to 8 parts by weight of fatty amine compound (B) per 100 parts by weight of polyamine compound (A) are mixed.
3. The curing agent for epoxy resin according to claim 1, wherein fatty amine (B) has at least 8 carbon atoms.
4. An epoxy resin composition consisting essentially of a curing agent for epoxy resin comprising polyamine compound (A) containing at least one compound selected from xylylenediamine, a modified product obtained by Mannich reaction of xylylenediamine and a phenolic compound or an aldehyde compound, a modified product obtained by the reaction of xylylenediamine and an epoxy compound, a modified product obtained by the reaction of xylylenediamine and a compound having a carboxyl group(s) and a modified product obtained by Michael reaction of xylylenediamine and an acrylic compound and a fatty amine compound (B) and an epoxy resin.

【0001】

【Industrially Applicable Field】

The invention relates to a curing agent for epoxy resin and a composition comprising said curing agent for epoxy resin and an epoxy resin, and specifically to a curing agent for epoxy resin and an epoxy

resin composition which are useful to coating materials to be used for corrosion prevention such as a coating, a flooring, a metal and concrete.

【0002】

【Prior Art】

Hitherto, various polyamine compounds have been widely known as a curing agent for epoxy resin. Particularly, aliphatic polyamine compounds have been widely known as a curing agent for epoxy resin to be cured at a room temperature. Such epoxy resin curing agent for epoxy resin to be cured at a room temperature provide uses such as a coating and a flooring. Among the above-mentioned aliphatic polyamines, xylylenediamine has a feature to provide a cured product in which low temperature curing property and chemical resistance are more excellent than other aliphatic polyamine compounds. However, xylylenediamine absorbs carbon dioxide and water vapor in the atmosphere to produce readily carbamate. Therefore, xylylenediamine has a defect that when it is used as a curing agent for epoxy resin, whitening of cured epoxy resin coating film occurs, so that the appearance of the coating film deteriorates and the interlayer adhesion of the coating film deteriorates. Further, there is a phenomenon that when water droplet is dropwise added on the coating film during cure, occurrence of whitening becomes intense on its portion.

【0003】

Therefore, xylylenediamine is seldom used in non-modification as a curing agent for epoxy resin and is used as various modified products in order to improve the above-mentioned defects. As typical method for modification, the following processes are known.

- (1) Modification by Mannich reaction with a phenolic compound and an aldehyde compound.
- (2) Modification by reaction with an epoxy compound.
- (3) Modification by reaction with a compound having a carboxyl

group(s).

- (4) Modification by Michael reaction with an acrylic compound.
- (5) Addition of a cure promoter such as a tertiary amine compound and a phenol compound.

However, the defects of xylylenediamine are not sufficiently overcome by the above-mentioned processes. Further, there is a problem that when a cure promoter is added as in (5), a time which it can be applied comes to be shortened, so that workability becomes bad.

【0004】

Further, there is a process for preventing absorption of carbon dioxide and water vapor in the atmosphere by covering a surface of a coating film using a paraffin wax in an unsaturated polyester resin. However, a paraffin wax has a defect that it is difficult to mix it with an epoxy resin and a curing agent for epoxy resin and when double coating is further applied on a coating film covered with a paraffin wax, failure of interlayer adhesion of the coating film, i.e., so-called interlayer peeling readily occurs. Thus, it is difficult to apply a paraffin wax to the field of an epoxy resin.

【0005】

【Problems to be Solved by the Invention】

An object of the invention is to provide a curing agent for epoxy resin which can overcome whitening of cured coating film and can prevent intense whitening to generate at the time of dropping water droplet on the coating film during cure and is excellent in interlayer adhesion in double coating, even when xylylenediamine or a modified product of xylylenediamine is used as a curing agent for epoxy resin.

【0006】

【Means for Solving the Problem】

As a result of extensive studies, the inventors have found that the

above-mentioned problems can be solved by using a curing agent for epoxy resin comprising xylylenediamine and/or a modified product of xylylenediamine and a fatty amine compound, and have accomplished the invention.

【0007】

That is, the invention relates to a curing agent for epoxy resin comprising a polyamine compound (A) containing at least one compound selected from xylylenediamine, a modified product obtained by Mannich reaction of xylylenediamine and a phenolic compound or an aldehyde compound, a modified product obtained by the reaction of xylylenediamine and an epoxy compound, a modified product obtained by the reaction of xylylenediamine and a compound having a carboxyl group(s) and a modified product obtained by Michael reaction of xylylenediamine and an acrylic compound and a fatty amine compound (B) and an epoxy resin composition consisting essentially of the curing agent for epoxy resin and an epoxy resin.

【0008】

The curing agent for epoxy resin to be used in the invention is a curing agent for epoxy resin comprising a polyamine compound (A) containing at least one compound selected from xylylenediamine, a modified product obtained by Mannich reaction of xylylenediamine and a phenolic compound or an aldehyde compound, a modified product obtained by the reaction of xylylenediamine and an epoxy compound, a modified product obtained by the reaction of xylylenediamine and a compound having a carboxyl group(s) and a modified product obtained by Michael reaction of xylylenediamine and an acrylic compound and a fatty amine compound (B).

【0009】

The polyamine compound (A) may be one compound selected from xylylenediamine, a modified product obtained by Mannich reaction of

xylylenediamine and a phenolic compound or an aldehyde compound, a modified product obtained by the reaction of xylylenediamine and an epoxy compound, a modified product obtained by the reaction of xylylenediamine and a compound having a carboxyl group and a modified product obtained by Michael reaction of xylylenediamine and an acrylic compound and a fatty amine compound (B) or at least two compounds thereof.

**[0010]**

Examples of xylylenediamine to be used in the invention include, typically, metaxylylenediamine.

**[0011]**

Examples of the modified product obtained by Mannich reaction of xylylenediamine and a phenolic compound and an aldehyde compound to be used in the invention include a reaction product of metaxylylenediamine and a phenolic compound and an aldehyde compound. Examples of the phenolic compound to be used for the above-mentioned modification include phenol, cresol, butylphenol, and nonylphenol. Examples of the aldehyde compound include formaldehyde, acetaldehyde and benzaldehyde. An aqueous solution of formaldehyde is usually used. The reaction ratio of metaxylylenediamine to a phenolic compound and an aldehyde compound in modification is not limited so long as it is a ratio wherein gelation can be avoided and a reaction product to be thus obtained contains an amino group with active hydrogen.

**[0012]**

Examples of the modified product of xylylenediamine and an epoxy compound to be used in the invention include a reaction product of metaxylylenediamine and an epoxy compound. Examples of an epoxy compound to be used for modification include monoepoxy compounds such as butyl glycidyl ether and phenyl glycidyl ether and diepoxy

compounds such as bisphenol A diglycidyl ether. The epoxy compound to be used for modification may be one kind of epoxy compound or a mixture of several kinds of epoxy resin. The reaction ratio of metaxylylenediamine to an epoxy compound in modification is not limited so long as it is a ratio wherein gelation can be avoided and a reaction product to be thus obtained contains an amino group with active hydrogen.

【0013】

Examples of the modified product of xylylenediamine and a compound having a carboxyl group(s) to be used in the invention include a reaction product of metaxylylenediamine and a compound having a carboxyl group(s). Examples of the compound having a carboxyl group(s) to be used for modification include dicarboxylic acids such as a polymerized fatty acid of so-called dimer acid, adipic acid and sebacic acid and monocarboxylic acids such as tall oil fatty acid, oleic acid and stearic acid. The reaction ratio of metaxylylenediamine to a compound having a carboxyl group(s) is not limited so long as it is a ratio wherein gelation can be avoided and a reaction product to be thus obtained contains an amine group with active hydrogen.

【0014】

Examples of the modified product obtained by Michael reaction of xylylendiamine and an acrylic compound to be used in the invention include a reaction product of metaxylylenediamine and a compound having a carbon-carbon double bond adjacent to a nitrile group or a carbonyl group. In detail, examples of the acrylic compound to be used for modification include acrylonitrile and methylmethacrylate. The reaction ratio of metaxylylenediamine to the acrylic compound is not limited so long as it is a ratio wherein gelation can be avoided and a reaction product to be thus obtained contains an amine group with active hydrogen.

**【0015】**

The polyamine compound (A) to be used in the invention may contain at least two kinds of the above-mentioned xylylenediamine and each modified product of xylylenediamine.

**【0016】**

Further, the polyamine (A) to be used in the invention may contain polyamine and each modified product of polyamine other than the above-mentioned xylylenediamine and each modified product of xylylenediamine. It is preferable that the content of other polyamine and other each modified product of xylylenediamine is a content not to impair the feature of xylylenediamine and the advantageous effects of the invention. It is preferably 50% by weight or below to total of polyamine compounds.

**【0017】**

The invention has a feature in that the fatty amine compound is contained in the curing agent for epoxy resin. The fatty amine compound (B) to be used in the invention is primary amine, secondary amine and tertiary amine compounds having preferably at least 8 carbon atoms which are produced using mainly fatty acid or higher alcohol as a raw material, among which a compound with primary amine is more preferable.

**【0018】**

The fatty amine compound (B) to be used in the invention has preferably at least 8 carbon atoms and its examples include primary amines compounds such as octylamine, dodecylamine, coconut alkylamine, tetradecylamine, hexadecylamine, octadecylamine, hardened beef tallow alkylamine, beef tallow alkylamine, oleylamine, soybean alkylamine and dimmer amine.

**【0019】**

The invention has a feature in that the curing agent for epoxy resin

contains fatty amine compound (B). However, in an amine compound having carbon atom below the above-mentioned range, it cannot be expected to overcome whitening of a coating film and to improve water resistance as the problems in the invention.

**【0020】**

It is preferable that the ratio of components in the curing agent for epoxy resin to be used in the invention i.e., a mixing ratio of polyamine (A) to fatty amine (B) is 2 to 8 parts by weight of fatty amine compound (B) per 100 parts by weight of polyamine (A). When a mixing ratio of fatty amine (B) is at least 2 parts by weight, it is possible to overcome whitening of a coating film and to improve water resistance. On the other hand, when it is 8 parts by weight or below, uniformity and transparency of the curing agent for epoxy resin can be maintained at a room temperature without impairing compatibility with polyamine compound (A).

**【0021】**

Further, where white turbidity of the curing agent for epoxy resin occurs at a room temperature depending on components of the curing agent for epoxy resin, uniform and transparent curing agent for epoxy resin is sometimes obtained at a room temperature by adding a third component in addition to polyamine compound (A) and fatty amine compound (B). Examples of the third component include benzyl alcohol and a reaction product of metaxylene and formaldehyde (manufactured by Mitsubishi Gas Chemical Co., Inc., trade name: Nicanol Y)

**【0022】**

The epoxy resin to be used in the invention is preferably liquid at a room temperature, i.e., at 15 to 30°C and its typical examples include a polymerization product of bisphenol A and epichlorohydrin and polymerization product of bisphenol F and epichlorohydrin. Reactive diluents such as butyl glycidylether and phenyl glycidylether or

non-reactive diluents such as benzyl alcohol may be contained in the epoxy resins. Further, a filler or a pigment may be contained in the curing agent for epoxy resin or the epoxy resin composition of the invention.

【0023】

【Example】

The evaluation methods of a coating film in Examples and Comparative Examples are described below.

Appearance:

Gloss, transparency and flatness are visually judged and evaluated.

Water resistance test:

After 1 day from coating and after 7 days from coating, an absorbent cotton dipped water is placed on a coating film and then after 1 day, the absorbent cotton is removed and change of the coating film surface is evaluated.

Interlayer peeling test:

After 7 days from coating of one layer, the same composition is again coated thereon and cured at 23°C for 7 days. Then, a test is conducted according to a cross cut test (JIS K 5400, space interval 2 mm/square number 25) to evaluate interlayer adhesion of coating film.

【0024】

The symbols for evaluation results of each coating films are represented below.

◎: excellent

○: good

△: a little bad

×: bad

State of whitening

EX: no whitening occurred

G: whitening slightly occurred

F: whitening occurred

P: whitening intensively occurred

**[0025] Reference Example 1**

272 g (2 mol) of metaxylylenediamine and 188 g (2 mol) of phenol were charged to a reaction vessel equipped with a stirrer, a thermometer, a nitrogen-introducing pipe, a reflux cooling tube, a dropping funnel and a water receiver. 108 g of formalin (a 8% methanol-containing 37% aqueous solution) was dropwise added thereto in a nitrogen gas flow with stirring at 90°C over about 1 hour. After the completion of dropwise addition, the interior temperature was raised to 100°C and the reaction was performed for 1.5 hours. The interior temperature was further raised to 15°C over 2 hours and the reaction was performed for one hour. The reaction product thus obtained was a light yellow and transparent liquid. The reaction product is denoted as amine A.

**[0026] Reference Example 2**

272 g (2 mol) of metaxylylenediamine was charged to a reaction vessel equipped with a stirrer, a thermometer, a nitrogen-introducing pipe, a reflux cooling tube, a dropping funnel and a water receiver. 152 g of bisphenol A diglycidyl ether (epoxy equivalent 190 g/eq) was dropwise added thereto in a nitrogen gas flow with stirring at 80°C over about 1 hour. After the completion of dropwise addition, the interior temperature was raised to 100°C and the reaction was performed for 2 hours. The reaction product thus obtained was a light yellow and

transparent liquid. The reaction product is denoted as amine B.

**[0027] Reference Example 3**

272 g (2 mol) of metaxylylenediamine and 231 g of dimmer acid (acid equivalent 289 g/eq) were charged to a reaction vessel equipped with a stirrer, a thermometer, a nitrogen-introducing pipe, a reflux cooling tube, a dropping funnel and a water receiver.

The reaction was performed for 1 hour at 180°C, for 1 hour at 200°C and for 2 hours at 230°C in a nitrogen gas flow with stirring and condensed water was distilled off. The reaction product thus obtained was a brown and transparent liquid. The reaction product is denoted amine C.

**[0028] Reference Example 4**

245 g of Amine C in Reference Example 3 was charged to a reaction vessel was charged to a reaction vessel equipped with a stirrer, a thermometer, a nitrogen-introducing pipe, a reflux cooling tube, and a dropping funnel in a nitrogen gas flow with stirring for 1 hour at 180°C and at 200°C. 67 g (0.28 mol) of P-S-butylphenylglycidyl ether was dropwise added thereto in a nitrogen gas flow with stirring at 80°C over about 1 hour. After the completion of dropwise addition, the interior temperature was raised to 100°C and the reaction was performed for 2 hours. The reaction product thus obtained was a brown and transparent liquid. The reaction product is denoted as amine D.

**[0029] Reference Example 5**

272 g (2 mol) of metaxylylendiamine was charged to a reaction vessel equipped with a stirrer, a thermometer, a nitrogen-introducing pipe, a reflux cooling tube and a dropping funnel. 53 g (1 mol) of acrylonitrile was dropwise added thereto in a nitrogen gas flow with stirring at 80°C over about 1 hour. After the completion of dropwise addition, the interior temperature was raised to 100°C and the reaction was performed for 2 hours. The reaction product thus obtained was a light

yellow and transparent liquid. The reaction product is denoted as amine E.

**【0030】 Reference Example 6**

272 g (2 mol) of metaxylylenediamine was charged to a reaction vessel equipped with a stirrer, a thermometer, a nitrogen-introducing pipe, a reflux cooling tube and a dropping funnel. 100 g (1 mol) of methylemethacrylate was dropwise added thereto in a nitrogen gas flow with stirring at 90°C over about 3 hours. After the completion of dropwise addition, the reaction was performed for 1 hour. The interior temperature was raised to 170°C over 1 hour and the reaction was further performed for 3 hours. The reaction product thus obtained was a light yellow and transparent liquid. The reaction product is denoted as amine F.

**【0031】**

Metaxylylenediamine or each polyamine compound shown in Reference Examples, a fatty amine compound and a diluent were mixed in each proportion shown in Tables 1 and 2 and were maintained to a uniform state with heating and cooled to a room temperature, whereby each curing agent for epoxy resin was prepared. Example Nos.1 to 13 for each curing agent for epoxy resin was numbered. Further, an epoxy resin and each curing agent for epoxy resin were mixed in each proportion shown in Tables 4 and 5 and the mixture thus obtained was coated on a cold rolled steel in a thickness of 200  $\mu$  m and cured for 7 days at 23°C, whereby each coating film was prepared. Evaluation of appearance, water resistance test, interlayer peeling test due to double coating were performed. The evaluation methods are as show below. The results are shown in Table 4 and 5.

**【0032】 Comparative Example 1 to 7**

As shown in Comparative Examples 1 to 7, each mixture of components adding no fatty amine compound was used as each curing

agent for epoxy resin and evaluated in the same manner as in Example 1. The result is shown in Table 6.

【0033】

【Effect of the Invention】

By using the curing agent for epoxy resin of the invention, whitening of a coating film which was a defect in conventional xylylenediamine type curing agent for epoxy resin can be overcome and an epoxy resin coating film excellent in both water resistance and interlayer adhesion can be obtained. Further, the coating film is excellent in gloss, transparency and flatness.

【0034】

Table 1 Components of curing agent for epoxy resin

Example No.	1	2	3	4	5	6	7
Components (weight ratio)							
MXDA 1)	95	—	—	—	—	—	—
Polyamine A	—	98	98	96	—	—	—
Polyamine B	—	—	—	—	98	96	96
Coconut alkylamine	—	2	—	—	—	—	—
Hexadecylamine	5	—	—	—	—	—	—
Octadecylamine	—	—	2	—	2	—	—
Oleylamine	—	—	—	4	—	4	—
Soybean alkylamine	—	—	—	—	—	—	4
Benzyl alcohol	25	—	25	—	25	—	—
Nicanol Y50	—	—	—	10	—	10	10

The abbreviation in Table 1) abbreviation of metaxylylenediamine

【0035】

Table 2 Components of curing agent for epoxy resin

Example No.	8	9	10	11	12	13
Components (weight ratio)						
Polyamine C	98	—	—	—	—	—
Polyamine D	—	95	98	92	—	—
Polyamine E	—	—	—	—	95	—
Polyamine F	—	—	—	—	—	98
Coconut alkylamine	—	8	—	—	—	—
Hexadecylamine	2	—	—	—	5	2
Octadecylamine	—	—	2	—	—	—
Benzyl alcohol	—	—	—	—	25	25

【0036】

Table 3 Components of curing agent for epoxy resin

Comp. Example No.	1	2	3	4	5	6	7
Components (weight ratio)							
MXDA 1)	100	—	—	—	—	—	—
Polyamine A	—	100	—	—	—	—	—
Polyamine B	—	—	100	—	—	—	—
Polyamine C	—	—	—	100	—	—	—
Polyamine D	—	—	—	—	100	—	—
Polyamine E	—	—	—	—	—	100	—
Polyamine F	—	—	—	—	—	—	100
Benzyl alcohol	25	25	25	—	—	25	25

The abbreviation in Table 1) abbreviation of metaxylylenediamine

【0037】

Table 4 Characteristics of coating film

Example No.	1	2	3	4	5	6	7
Blend of Resin (weight ratio)							
Epoxy resin main gradient 1)	100	100	100	100	100	100	100
Curing agent for epoxy resin	22	37	47	47	41	39	34
Evaluation of coating film							
Appearance: State of whitening	EX	EX	EX	EX	EX	EX	EX
Gloss	◎	◎	◎	◎	◎	◎	◎
Transparency	◎	◎	◎	◎	◎	◎	◎
Flatness	◎	◎	◎	◎	◎	◎	◎
Water resistance: after 1 day	◎	◎	◎	◎	◎	◎	◎
after 7 days	◎	◎	◎	◎	◎	◎	◎
Interlayer adhesion	◎	◎	◎	◎	◎	◎	◎

【0038】

Table 5 Characteristics of coating film

Example No.	8	9	10	11	12	13
Blend of Resin (weight ratio)						
Epoxy resin main gradient 2)	100	100	100	100	100	100
Curing agent for epoxy resin	41	56	56	56	43	46
Evaluation of coating film						
Appearance: State of whitening	EX	EX	EX	EX	EX	EX
Gloss	◎	◎	◎	◎	◎	◎
Transparency	◎	◎	◎	◎	◎	◎
Flatness	◎	◎	◎	◎	◎	◎
Water resistance: after 1 day	◎	◎	◎	◎	◎	◎
after 7 days	◎	◎	◎	◎	◎	◎
Interlayer adhesion	◎	◎	◎	◎	◎	◎

The abbreviation in Table 2) abbreviation of bisphenol A glycidyl ether (epoxy equivalent 190g/eg), which is the same also in Table 6

【0039】

Table 6 Characteristics of coating film

Example No.	1	2	3	4	5	6	7
Blend of Resin (weight ratio)							
Epoxy resin main gradient	100	100	100	100	100	100	100
Curing agent for epoxy resin	22	48	40	41	56	43	46
Evaluation of coating film							
Appearance: State of whitening	P	G	G	F	F	F	F
Gloss	△	◎	○	△	△	△	○
Transparency	×	○	○	△	△	△	△
Flatness	○	○	○	△	○	○	△
Water resistance: after 1 day	×	△	△	△	△	△	△
after 7 days	△	△	△	△	△	△	△
Interlayer adhesion	×	○	○	△	△	△	△